

**Sulfur K-edge X-ray Absorption Near-Edge Structure (XANES) spectroscopy as a tool for understanding sulfur dynamics in soil organic matter following land use changes**

D. Solomon, J. Lehmann (Cornell University), and C.E. Martinez (Penn State University)

Beamline: X19A

**Introduction:** The soil environment is the primary component of the global biogeochemical S cycle, acting as a source and sink for various S species and mediating changes of oxidation states. Most of the soil S (> 95%) is present in organic forms [1, 2]. Speciation of S in organic materials could, therefore, provide a clear understanding of the amount, form and biogeochemical transformations of S in the ecosystem. Our knowledge of the biogeochemical S cycling is, however, severely limited by relatively crude analytical techniques used in S measurements and speciation. Most of the present studies on soil S are based on a fractionation technique using hydroiodic acid (HI) reduction of organic S compounds in soil [3]. However, this technique to characterize soil S is only an indirect method involving differential reduction of various organic S compounds to H<sub>2</sub>S and is therefore not an entirely satisfactory procedure to directly speciate S within complex organic functional groups [1].

**Methods and Materials:** Samples were dried and sieved to pass 2mm and measured directly or extracted. Three different methods were used for the extraction: (i) the classic humic acid extraction, (ii) NaOH+NaF extraction, and (iii) NaOH+NaF extraction followed by filtration to 0.2 micrometers under pressure to remove fine particles. The XANES measurements were conducted under the standard operating conditions i.e., the K-edge of the spectrum will be assigned an energy value of 2472 eV and scans ranged from 50 eV below to 150 eV above the absorption edge of S with a step size of 0.2 eV. Each XANES spectrum is composed of two scans. A monochrome consisting of double crystal Si (111) was used with an entrance slit of 0.5 mm and minimum energy resolution of  $2 \times 10^{-4}$  (0.5 eV) at the S K-edge. The spectra were recorded in fluorescence mode using a passivated implanted planar silicon (PIPS)-detector. The beam path from incident ion chamber to the sample chamber was purged with helium gas. The samples were pressed into thin films by using 0.5 cm thick acrylic holder and covered with Mylar film (2.5 micro-m thick, Complex Industries NY).

**Results:** The analyses of whole mineral soil proved to have low signal-to-noise ratios and spectra could not be quantitatively analyzed (Fig. 1). NaOH+NaF extraction and additional filtration of the extract significantly improved signal intensities (Fig. 1). The much simpler NaOH+NaF extraction yielded more organic matter in the extract and similar results and was therefore preferred over the traditional humic acid extraction. A qualitative comparison between the spectra of the whole soil and the extract showed only minor differences. Therefore, oxidation states determined from extracts can be taken as an adequate representation of the entire soil. Sulfur oxidation states significantly changed when natural forest soil was disturbed and either tree or annual crops were grown (Fig. 2). With more intensive disturbances of the soil ecosystem, oxidized S increased and reduced S decreased. Since inorganic S contents were less than 2% of the total S [2], the changes in oxidation states apply to organic S.

**Conclusions:** Sulfur forms in soil determined by S K-edge XANES revealed important changes in the biogeochemistry of soil S, in contrast to methods applied before. This new understanding needs to be linked to C chemistry and biology to evaluate controls of S on the C cycle in soil.

**Acknowledgments:** Many thanks to Wolfgang Caliebe for the excellent support. National Synchrotron Light Source (NSLS) is supported by the U.S. Department of Energy under the contract No. DE-AC02-76CH00016.

**References:**

- [1] H.H. Janzen and B.H. Ellert, "Sulfur dynamics in cultivated temperate agroecosystems," In: D.G. Maynard (ed.) *Sulfur in the Environment*. Dekker, New York, pp. 11-43. (1998)
- [2] D. Solomon, J. Lehmann, M. Tekalign, F. Fritzsche, and W. Zech, "S fractions in particle-size separates of the subhumid Ethiopian highlands as influenced by land use changes," *Geoderma* **102**, 42-59. (2001)
- [3] M.A. Tabatabai, "Sulfur," In: C.A. Black (ed.) *Methods of Soil Analysis, Part 2, Chemical and Microbial Properties*. Agron. Mono., No. 9, ASA-SSSA, Madison, Wisconsin, pp. 501-538. (1982)

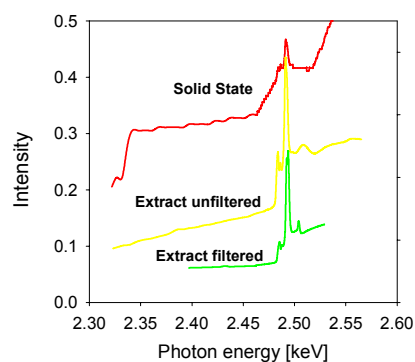


Fig. 1: Sulfur K-edge XANES spectra obtained from whole soil and soil extracts (NaOH+NaF).

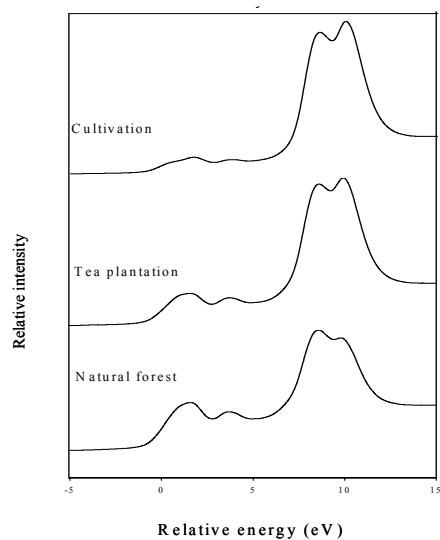


Fig. 2: Sulfur K-edge XANES spectra of soil extracts of clay size separates obtained from cultivated fields and fields under tree plantations in comparison to primary forest in Ethiopia.